Name: Key

Discussion Section: (Janette, Peter, Richard, Stephen)

Note: V_A & V_B not necessarily equal so, n_A & n_B are ~~SID~~ not necessarily equal even though P & T are constant.

1. (15 pts) The following problems involve thinking about entropy and free energy.

a) Let the amounts of gases in two containers be n_A and n_B; both are at pressure, p, and temperature T. The chemical potential of gas A is μ_A and that of B is μ_B.

Write down the total free energy of this system in terms of the chemical potentials. Write down the chemical potentials in terms of the standard chemical potentials and the pressures. Remember to check your units!

5pts.

$$G_{unmixed} = G_A + G_B$$
$$= n_A\mu_A + n_B\mu_B$$
$$= n_A(\mu_A^\circ + RT\ln a_A) + n_B(\mu_B^\circ + RT\ln a_B)$$
$$\boxed{= n_A\left(\mu_A^\circ + RT\ln\frac{P_A}{1atm}\right) + n_B\left(\mu_B^\circ + RT\ln\frac{P_B}{1atm}\right)}$$

where $P_A = P_B = P$

Imagine now that the partition between the two containers is removed. Write down the equation for the new total free energy.

2pts.

$$G_{mixed} = G_A^* + G_B^*$$
$$\boxed{= n_A\left(\mu_A^\circ + RT\ln\frac{P_A^*}{1atm}\right) + n_B\left(\mu_B^\circ + RT\ln\frac{P_B^*}{1atm}\right)}$$

new partial pressures. Not necessarily equal. (see above expl.)

Write down the equation for ΔG_{mixing} for this process.

recall, $a\ln x = \ln x^a$

2pts.

$$\Delta G_{mixing} = G_{mixed} - G_{unmixed}$$
$$= RT\ln\left(\frac{P_A^*}{1atm}\right)^{n_A} + RT\ln\left(\frac{P_B^*}{1atm}\right)^{n_B} - RT\ln\left(\frac{P_A}{1atm}\right)^{n_A} - RT\ln\left(\frac{P_B}{1atm}\right)^{n_B}$$
$$\boxed{= RT\ln\left(\frac{P_A^*}{P}\right)^{n_A}\left(\frac{P_B^*}{P}\right)^{n_B}}$$

recall $\ln x - \ln y = \ln\left(\frac{x}{y}\right)$, $\ln x + \ln y = \ln(xy)$

Write the equation in terms of mole fractions and determine the sign of ΔG_{mixing}.

2 pts.

Using ideal gas law: $n_A = \frac{P_A^* V}{RT}$, $n_{tot} = \frac{PV}{RT}$

therefore: $\frac{n_A}{n_{tot}} = \frac{P_A^*}{P}$

so, $$\boxed{\Delta G_{mixing} = RT\ln\underbrace{\left(\frac{n_A}{n}\right)^{n_A}\left(\frac{n_B}{n}\right)^{n_B}}_{<1 \text{ always}}}$$

Since $\ln x$ is negative for $x<1$, ΔG_{mixing} is negative.

Write the equation for ΔS_{mixing} for the same system and what is the sign?

4 pts.

$$\Delta S_{mixing} = -\left(\frac{\partial \Delta G_{mixing}}{\partial T}\right)_P = \frac{-\partial}{\partial T}\left[RT\ln\left(\frac{P_A^*}{P}\right)^{n_A}\left(\frac{P_B}{P}\right)^{n_B}\right]$$
$$\boxed{= -R\ln\underbrace{\left(\frac{P_A}{P}\right)^{n_A}\left(\frac{P_B}{P}\right)^{n_B}}_{<1}}$$

ΔS_{mixing} is always positive.

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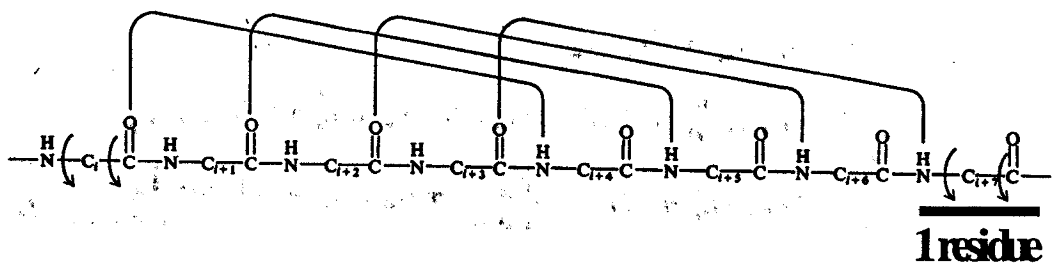
2. **(15 pts)** It is well known that polypeptides can adopt an α-helical conformation in solution. It is known that small changes in temperature can cause this structure to unfold in some cases. Of interest to the structural biologist is what proportion of chains in solutions are helical and which are "denatured (coiled)." Each polypeptide has only two states: completely helical or completely denatured.

6 pts

a) In forming an α-helix, n-residues long the carboxy-group of one residue forms a hydrogen bond with the amino-residue 4 residues up-stream of it.

10



The free energy for converting a given residue in the helix from its free to its hydrogen bonded state is ΔG_h. This free energy is composed of the enthalpy of forming a hydrogen bond (per residue) and the change in (conformational) entropy that occurs when the bond is formed. **What is the expression for the <u>total</u> free energy change for converting a "denatured" polypeptide of length n to a helical polypeptide in terms of ΔG_h and ΔS_h?** ***(Hint:*** Remember to consider the end-effects-- four amino groups on the left are unbonded and the terminal residues of each chain are never conformationally restricted.)

$\because \Delta G_h = \Delta H_h - T\Delta S_h$ for <u>each</u> residue & there are n residues.

coefficient for ΔH: THERE ARE $(n-4)$ H Bonds & $(n-4)$ O-Bonds but we only COUNT EACH BOND ONCE, SO $\frac{(n-4)+(n-4)}{2} = \underline{n-4}$

coefficient for ΔS: THERE ARE 2 terminal ends, so $(n-2)$ residues are CONFORMATIONALLY RESTRICTED $\Rightarrow$ $\underline{(n-2)}$

$$\Delta G_{TOT} = \sum_i \Delta G_{h,i} = (n-4)\Delta H_h - (n-2)(T)\Delta S_h$$

1 pt for writing $\Delta G = \Delta H - T\Delta S$

1 pt for recognizing ~~that these~~ the dependency on n

2 pts each for getting proper coefficients for ΔH_h & ΔS_h

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b) A researcher working on a particular helix-coil transition measures the following data.

9 pts

T(K)	324.4	326.1	327.5	329.0	330.7	332.0	333.8
Keq	0.041	0.12	0.27	0.68	1.9	5.0	21

6pts Calculate ΔG° for this transition at 54.5 C. Estimate a value ΔH for the transition at this temperature.

$$54.5^\circ C = 327.5\,K$$

i) $$\Delta G = -RT\ln K = -\frac{8.314\times10^{-3}\,kJ}{mol\cdot \cancel{K}}(327.5\cancel{K})\ln 0.27 = 3.565\,kJ/mol$$

3 pts for correct answer
2 pts off for not using 327.5 K
1 pt off for each: NO UNITS, INCORRECT sign, MATH ERROR

ii) $$\ln\frac{K_2}{K_1} = \frac{-\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \Rightarrow \Delta H = -R\cdot\ln\left(\frac{K_2}{K_1}\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}$$

using any two values above for K_1/K_2 & T_1/T_2... (I used 329K & 327.5K)

$$\Delta H = -\frac{8.314\times10^{-3}\,kJ}{mol\cdot\cancel{K}}\cdot\ln\left(\frac{0.68}{0.27}\right)(-7.18\times10^{4}\cancel{K}) = 552\,kJ\,mol^{-1}$$

3 pts for correct answer
1 pt off for each: NO UNITS, INCORRECT MATH, INCORRECT SIGN

3pts How would you then calculate ΔS_{TOT}?

We were not expecting a numerical answer because IT IS ONLY AN ESTIMATE.

$$\Delta G_{TOT} = \Delta H_{TOT} - T\Delta S_{TOT} \Rightarrow \Delta S_{TOT} = \frac{\Delta H_{TOT}-\Delta G_{TOT}}{T}$$

you COULD HAVE ALSO gone through the derivation from part a, but it was not necessary. ALSO, ANSWERS USING the relation $\Delta G = -RT\ln K$ were acceptable.
points off for making a math error

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3. (15 pts) Cells need to maintain a difference (gradient) in chemical concentrations across their membrane. To do this they use a number of different mechanisms including simple pores and specific chemical transport proteins.

Imagine a particular (nonionic) species maintains a concentration of c1 outside the cell and a concentration of c2 inside the cell.

6pts total.

What is the expression for the free energy change for transporting this species from the outside to the inside of the cell?

$G(C_1) = G^\circ + RT\ln C_1$ $G(C_2) = G^\circ + RT\ln C_2$

$\boxed{\Delta G = RT\ln\frac{C_2}{C_1}}$ or $RT\ln\frac{[\text{inside}]}{[\text{outside}]}$.

+6 point if perfect. +3 point total if sign is wrong or extra term.

5 pts total.

It is found for this species that the concentration outside the cell in 1 μM and the concentration inside the cell 1 mM. Is this process spontaneous? (Explain based on the equation and common sense.)

$\Delta G = RT\ln\frac{1\times10^{-3}M}{1\times10^{-6}M} = RT\ln(1\times10^{3}) =$ positive number.

Not spontaneous.

+ 5 point for correct with good explaination.

+ 1 point only if only the first step is written.

What two things would we have to consider if the species were ionic in calculating the free energy?

+2pts

1st: For ionic species, $a \neq c$. Thus γ activity coefficient is important to consider.

+2pts

2nd: Ionic species is charge particule.
Thus there is a electrical potential gradient across the cell membrane (not just chemical potential) Need to consider $\vec{E}$ or V.

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4. (15 pts) At the core of the electron transport chain that drives respiration is the electron transfer potential of NADH or $FADH_2$ relative to that of oxygen.

(a) What is the difference between the biochemist's and chemist's standard state? Write down the overall reaction for the reduction of oxygen by NADH. Calculate the standard free energy of this reaction? Calculate the equilibrium constant? (Use the biochemist's standard state for calculations!)

$$\boxed{\begin{array}{ll} \text{Biochemist's}: & pH = 7 \\ \text{Chemist's}: & pH = 0 \end{array}}$$

Half-Reactions

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O \qquad (0.82V)$$

$$- \quad NAD^+ + H^+ + 2e^- \longrightarrow NADH \qquad (-0.32V)$$

$$\boxed{\frac{1}{2}O_2 + H^+ + NADH \longrightarrow H_2O + NAD^+ \qquad (1.14V)}$$

$$\Delta G = -nF\mathcal{E} = -2 \cdot \left(9.65 \times 10^4 \frac{C}{mol}\right) \cdot \left(1.14 \frac{J}{C}\right)$$

$$= -220 \times 10^3 \frac{J}{mol} = \boxed{-220 \frac{kJ}{mol}}$$

$$K = e^{\frac{-\Delta G}{RT}} = \exp\left(+220 \frac{kJ}{mol} \Big/ 2.5 \frac{kJ}{mol}\right) = \boxed{1.65 \times 10^{38}}$$

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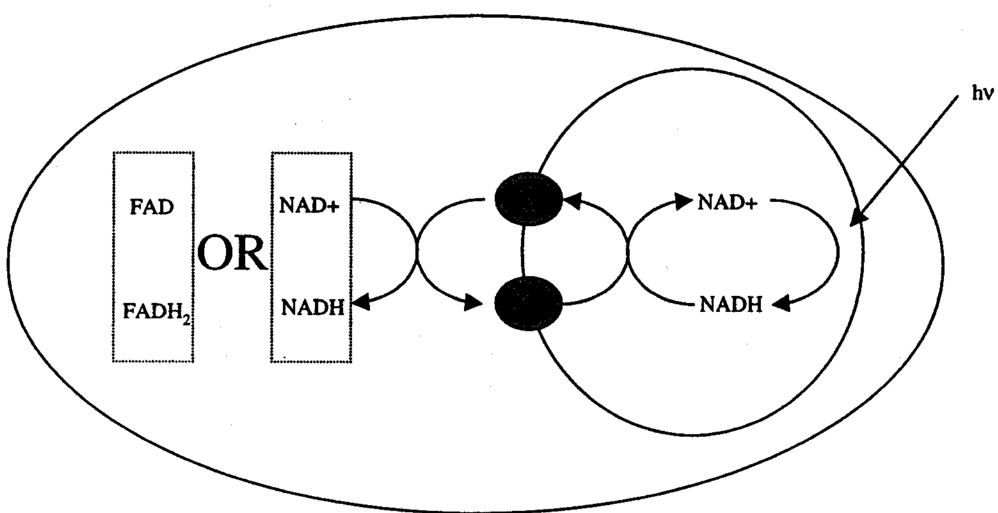
Bonus problem: 10 pts

Imagine the following cell in which NADH is generated by a photosynthetic process in a small organelle inside a cell. In turn, the NADH is used to reduce a protein in the organelle membrane and then this protein supposedly reduces either NAD^+ or FAD^+ in the cytoplasm. Imagine that this cell is illuminated such that the $NADH/NAD^+$ ratio in the organelle is maintained at 10:1. With all else at equilibrium (and at 37 °C) what ratio of $NADH/NAD^+$ can be maintained in the cytoplasm? What ratio of $FADH_2/FAD$ can be maintained in the cytoplasm? Show all how all half reactions contribute.



$[NADH]/[NAD^+] = 10:1$

$[FADH_2]/[FAD] = 19213 : 1$